

Fractal properties of clusters of colloidal magnetic particles

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We have studied the properties of clusters of colloidal magnetic particles generated from a 2D aggregation model with dipolar interparticle interactions. Particles diffuse off-lattice, experiencing dipolar interactions with the already attached particles until either they stick to the cluster or wander far away and are removed. Our results are interpreted in terms of a fractal dimension that is a monotonically decreasing function of the temperature, varying between a definite value close to 1 at $T = 0$, and the limit $T \rightarrow \infty$, corresponding to free diffusion-limited aggregation. By analyzing orientational correlation functions, an ordered state is found at low temperatures; this state is destroyed by the fractal disorder generated at high T . Our study could be relevant in understanding aggregation of dipolar colloids and phase transitions in Langmuir monolayers.

I. INTRODUCTION

Fractal growth phenomena [1] have been a particularly active field of physics in the last decade, due to the potential applications to many disciplines, in particular to the physics of colloids. In the context of computer models, the most noteworthy are the diffusion-limited aggregation (DLA) model [2] and the cluster-cluster aggregation model [3], which indeed can describe the fractal structure of colloidal aggregates [4].

Most often the above mentioned models assume very short range interparticle interactions; usually a hard-core potential plus an infinite well on the surface of the particles. They are therefore appropriate to describe aggregation with interactions strongly decaying with distance. However they fail to represent aggregation in the presence of long-range forces. Some examples of such kind of processes are the aggregation of particles subject to *dipolar forces*. Actual experiments have been conducted in ferrofluids and the so-called magnetic holes [5]; part of their interest lies in the extreme simplicity of the experimental setup, which can be easily performed with magnetized microspheres [6]. On the other hand, there is a considerable interest in the study of phase transitions in Langmuir monolayers [7]. Far from equilibrium, the condensed phase grows at the expense of the liquid phase, forming clusters of different shapes. The phospholipids constituting the Langmuir monolayer experience repulsive dipolar interactions, which must play a major role in determining the morphology of the condensed aggregates.

Some authors have extended the classic models in order to take interparticle interactions into account. The modifications proposed so far are either deterministic [8,9] or random [10–13], using Monte Carlo or Langevin dy-

namics methods. However, because the implementation of long range interactions is extremely time-consuming, only modest-sized aggregates can be grown (up to 128 particles in [9,14,15]). Therefore the results do not allow categorical conclusions to be made about the fractal properties of the dipolar clusters.

Our purpose in this paper is to extend the particle-cluster aggregation model in order to include fully anisotropic attractive dipolar interparticle interactions. Our algorithm is considerably fast, allowing us to generate clusters up to 10000 particles at zero temperature, in a reasonably short time. In Section II we describe the technical details of the algorithm. Section III discusses the evolution as a function of temperature of the fractal dimension and the order induced on the orientation of the dipoles by their reciprocal interactions. Our conclusions are discussed finally in Section IV.

II. CLUSTER FORMATION ALGORITHM

We consider the two-dimensional aggregation process of magnetic particles of diameter d and magnetic moment $\vec{\mu} = \mu \vec{u}$, with μ being the magnetic moment strength and \vec{u} a unit vector oriented along its direction. The dipolar energy between two particles i and j , located at the positions \vec{r}_i and \vec{r}_j , respectively, is $\mathcal{E}_{ij} = \mu^2 E_{ij}$, E_{ij} being the dimensionless dipolar energy

$$E_{ij} = \{\vec{u}_i \cdot \vec{u}_j - 3(\vec{u}_i \cdot \vec{r}_{ij})(\vec{u}_j \cdot \vec{r}_{ij})/r_{ij}^2\} / r_{ij}^3, \quad (1)$$

and $\vec{r}_{ij} = \vec{r}_i - \vec{r}_j$.

The simulation starts with a seed particle located at the origin of coordinates, bearing a randomly oriented tridimensional vector \vec{u}_1 , parallel to the plane of growth.

The following particles are released from a random position on a circle of radius R_{in} centered on the seed. The particles have assigned a vector \vec{u}_i oriented at random. Each particle undergoes a random walk until it either contacts the cluster or moves away from the origin a distance greater than R_{out} . In this case, the particle is removed and a new one is released from the circle surrounding the seed. We have used the values $R_{\text{in}} = 2R_{\text{max}} - 5$ and $R_{\text{out}} = 2R_{\text{max}}$, where R_{max} is the maximum radius of the cluster. The random walk experienced by the incoming particles is affected by the interactions exerted by the particles already attached to the cluster. We have taken this fact into account by using a Metropolis algorithm inspired by Refs. [14,15]. Suppose that the cluster is composed by $n - 1$ particles, placed at the points \vec{r}_i , $i = 1, \dots, n - 1$. At some time t the incoming particle occupies the position \vec{r}_n and has an interacting energy $E = \sum_{i=1}^{n-1} E_{ni}$. At time $t + 1$ we compute a new position \vec{r}_n^* ; the particle arrives there by means of jump of length d in a direction chosen at random. The movement to \vec{r}_n^* is performed rigidly, without changing \vec{u}_n . The energy experienced in the new position is E^* , and the total change in the energy due to the movement is $\Delta E = E^* - E$. If $\Delta E < 0$, then the movement is accepted; if $\Delta E > 0$, we compute the quantity $p = \exp(-\Delta E/T_r)$, where

$$T_r = \frac{d^3 k_B T}{\mu^2}. \quad (2)$$

(T_r is a *reduced temperature*, related to the intensity of the interaction and the actual temperature T .) In this latter case, the movement is accepted with probability p . After every accepted movement, the moment of the random walker is oriented along the direction of the total field on its position. This fact indeed assumes that the relaxation time for the orientation of particles is very short in comparison with the movement of the center of mass. The particle sticks to the cluster when it overlaps one or more particles already incorporated. After sticking, the newly attached particle undergoes one last relaxation.

III. FRACTAL PROPERTIES OF THE CLUSTERS

The purpose of this Section is to analyze the fractal properties of the clusters generated using the prescription outlined above. In Fig.1 we have represented typical clusters of 1000 particles, grown at four different values of T_r . The effects of temperature can be seen by comparing with a pure non-interacting DLA cluster, as shown in Fig.1(d). At low T_r , Fig.1(a), the dipolar clusters have a lesser branched and more open structure, that is to say, they have a smaller ratio of bifurcation. Even though the clusters may seem to be anisotropic, they still possess spherical symmetry: When collapsing an ensemble of clusters at the same T_r , we recover a perfectly symmetric structure. When increasing the temperature, the branching of the clusters increases correspondingly;

for $T_r = 10$ (the largest value simulated), Fig.1(c), the clusters are completely indistinguishable from true DLA.

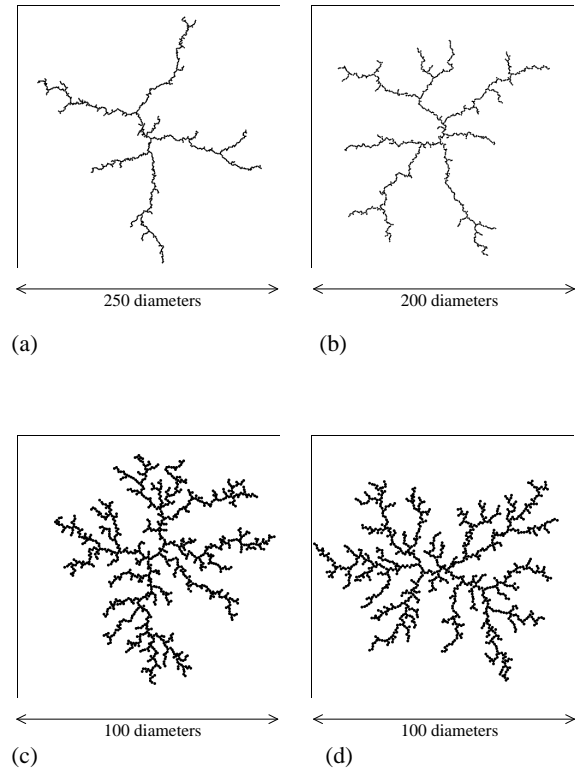


FIG. 1. Typical 2D dipolar clusters of 1000 particles, generated for several values of T_r . (a) $T_r = 0$, $D = 1.20 \pm 0.02$. (b) $T_r = 10^{-3}$, $D = 1.35 \pm 0.04$. (c) $T_r = 10$, $D = 1.74 \pm 0.02$. (d) Pure DLA cluster, grown in the limit $T_r \rightarrow \infty$, $D = 1.71 \pm 0.01$.

In order to quantify this temperature dependence, we have computed the fractal dimension D of the clusters, determined from a log-log plot of the radius of gyration as a function of the number of particles N [1],

$$R_g(N) = \left(\frac{1}{N} \sum_{i=1}^N (\vec{r}_i - \vec{r}_{\text{c.m.}})^2 \right)^{1/2} \sim N^{1/D}. \quad (3)$$

The algorithm was checked by computing the dimension of an ensemble of 100 clusters of 1000 particles, generated in the limit $T_r \rightarrow \infty$ (pure DLA). The value computed was $D = 1.71 \pm 0.01$; we recover, within the error bars, the well-known result $D = 1.715 \pm 0.004$ [16].

Fig.2 shows a plot of D as a function of T_r for the whole range of values analyzed. It seems to exhibit a *smooth* increasing behavior when increasing T_r , the values of D ranging between the limits corresponding to $T_r = 0$ (aggregation with dipolar forces of infinite strength or zero temperature) with $D = 1.13 \pm 0.01$ and $T_r = \infty$ (aggregation with no interactions or infinite temperature), with $D = 1.71 \pm 0.01$. We can compare our results with the colloidal aggregation experiment described in [15], where magnetic particles were employed for which $T_r^{-1} \simeq 1360$

at room temperature. In our simulations, the fractal dimension obtained for clusters grown at $T_r = 10^{-3}$ is $D = 1.35 \pm 0.04$, a value clearly different from the one computed at $T_r = 0$.

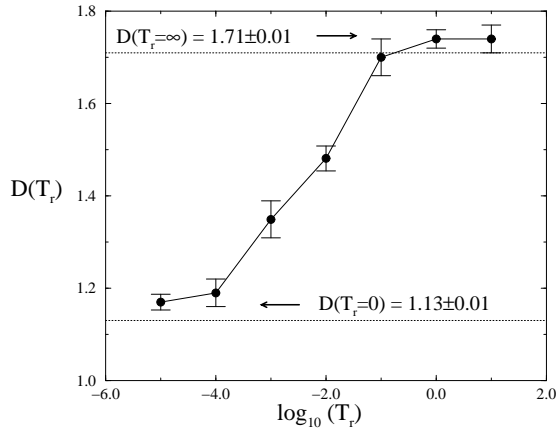


FIG. 2. Fractal dimension D as a function of T_r for dipolar clusters.

The shape of Fig.2 can be explained as follows. Given the expression (1) for the dipolar energy, it is energetically favorable for an incoming particle to stick at the tip of a branch, contributing thus to its growth, rather than sticking on any side and splitting it. At low temperatures, therefore, the most probable scenario is that of a cluster with a very small branching ratio and a low fractal dimension. This is consistent with the fact that, at $T_r = 0$, the fractal dimension seems to decrease when increasing N ; we cannot even reject the possibility of a dimension equal to 1 in the limit $N \rightarrow \infty$. On the other hand, at large temperature the growth of a given branch and its split are equally likely events. The effect of dipolar interactions is overcome by thermal disorder and we recover the original DLA model with no interactions. At intermediate values of T_r , there would be a competition between growth and splitting, ruled by the thermal disorder as well as the dipolar interactions. We should then expect a continuous change in the geometry of the cluster and, therefore, a smooth dependence of D on the temperature.

The fractal dimension we have considered so far is a *macroscopic* property of dipolar aggregates. However, their composing particles also bear a rigid magnetic dipole, which confers a *microscopic structure* to the clusters. In order to obtain information about this structure, we have analyzed the *relative orientation* between pairs of dipoles. To this end, we define the function $g_T(\theta)$ as the probability density that the relative angle formed by the directions of a pair of dipoles randomly chosen from a cluster at temperature T_r is included in the interval $[\theta, \theta + d\theta]$; θ is defined to be normalized to the interval $[0, \pi]$. In practice, if $n(T_r, \theta)$ is the number of pairs with

a relative angle between θ and $\theta + \Delta\theta$, for a fixed angular increment $\Delta\theta$, then we have

$$g_T(\theta) = \frac{2}{N(N-1)} \frac{1}{\Delta\theta} n(T_r, \theta), \quad (4)$$

N being the number of particles in the cluster. g_T is a measure of the order of the dipoles on the cluster. In a completely disordered distribution, all relative orientations are equally probable and, therefore, we have $g(\theta) = 1/\pi$. On the other hand, in a distribution in which all the dipoles point in the same direction (for example, in the presence of a strong magnetic field) every pair forms a relative angle of zero radians, and thus $g(\theta) = \delta(\theta)$.

Fig.3 depicts $g_T(\theta)$ computed from several ensembles of clusters grown at different values of T_r , between 0 and 10.

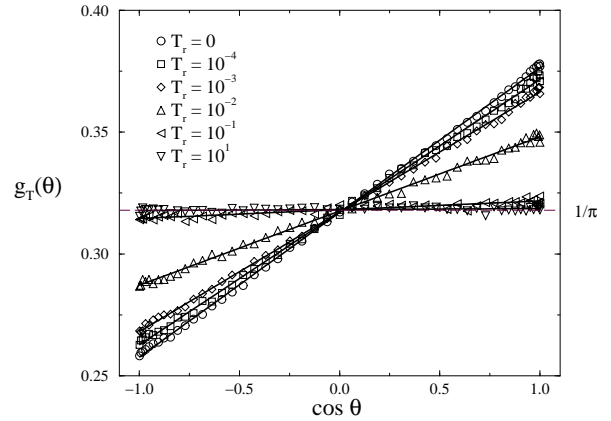


FIG. 3. Orientational correlation $g_T(\theta)$ as a function of $\cos \theta$, computed for dipolar clusters at different values of T_r . At high temperatures the slope is almost zero. Solid lines are least-squares fittings.

Numerically we observe that $g_T(\theta)$ fits extremely well to the function

$$g_T(\theta) = a + b(T_r) \cos \theta. \quad (5)$$

The normalization condition of g_T implies obviously $a = 1/\pi$, as observed. On the other hand, $b(T_r)$ seems to be a decreasing function of temperature, between the limits $b(0) = 0.0594 \pm 0.0005$ and $b(\infty) \sim 0$. The slope $b(T_r)$ can be seen as a measure of the degree of internal order in the orientation of the dipoles in the cluster. In the low temperature limit (in the absence of any thermal disorder) the orientation of the dipoles is strongly correlated, and this fact is reflected in a nonzero slope b . As temperature raises, $g_T(\theta)$ decreases continuously. In the high temperature limit dipoles show a large disorder, imposed by the intrinsic fractal geometry, and the function g_T is almost flat (all relative orientations are equally probable). Once again, the apparently continuous variation of

g_T hints towards a smooth dependence of the geometry of the clusters on the temperature.

IV. CONCLUSIONS

We have investigated the effects of dipolar interactions in particle-cluster aggregation in two dimensions. The relevant parameter in the model is the dimensionless temperature T_r defined in (2), which relates the real temperature T and the strength of the magnetic interactions μ . At low temperatures we observe clusters with a less branched and more open structure than free DLA, and correspondingly, a fractal dimension close to 1. This is an effect of the dipolar interaction on the local growth-site probability distribution [1]. The growth of a given branch is a more likely event than its split, resulting in an enhancement of the screening of the inner regions. At high temperatures the fractal dimension raises its value until it reaches the limit of free DLA. The plot of D as a function of T_r , Fig.2, seems to show a smooth behaviour, resulting from the competition between dipolar attractive forces and thermal disorder. The internal structure of the clusters, probed through the function g_T , seems also to show a smooth transition between an ordered state at low temperature, with long range correlations between dipoles, and a disordered state at high temperature, in which all relative orientations are equally probable. This loss of order is explained as the effect of the geometrical disorder induced by the fractal character of the clusters. Our results could be relevant to understand the processes of cluster aggregation in dipolar colloids. Even though our result are relative to attractive dipolar interactions, they could also be applied to study cluster growth in Langmuir monolayers; the similarity with experimental clusters has already been pointed out in Ref. [13], in the particular case of *isotropic* dipolar interactions (potential decaying with distance as r^{-3}).

As a final remark, we would point out that, even though all our results are consistent with a geometry continuously varying with the temperature, they are also compatible with a different scenario, in which there is sharp crossover between the low temperature dimension $D_0 \simeq 1.13$ and the high temperature dimension $D_\infty \simeq 1.71$. From Fig.2, the crossover temperature could be estimated to be $T_c \simeq 10^{-3.5} \sim 3 \times 10^{-4}$. The presence of the sharp fall in D would then be smoothed out by finite-size effects, unavoidable for the cluster sizes we are considering. Further work should be done in order to elucidate this possibility, especially by simulating aggregates larger than those actually available with our present computer resources.

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